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(54) Title: <b>PREPARING A HIGH VISCOSITY INDEX, LOW BRANCH INDEX DEWAXED OIL</b>			
(57) Abstract			
<p>An integrated process for preparing a lubricating oil base stock includes an isomerization step followed by a solvent dewaxing step. A waxy feed is isomerized to an intermediate pour point, which is at least 6 °C above a target pour point, over a select molecular sieve having specified pore properties. The isomerized oil is then solvent dewaxed to a very low pour point. This process produces a dewaxed lubricating oil base stock which has an exceptionally high viscosity index.</p>			
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1                   **PREPARING A HIGH VISCOSITY INDEX,**  
2                   **LOW BRANCH INDEX DEWAXED OIL**

3           This patent application claims priority from U.S. Provisional Patent  
4   Application Serial No. 60/077070, filed March 6, 1998, the specification of  
5   which is incorporated herein by reference for all purposes.

6                   **BACKGROUND OF THE INVENTION**  
7

8           The present process is a dewaxing process for producing very high  
9   viscosity index, low pour point lubricating oil base stocks from a mineral oil  
10   feed. When preparing a lubricating oil base stock from a mineral oil, viscosity  
11   index is generally increased to a target value during an upgrading step using  
12   hydrocracking, solvent refining, etc. Pour point is generally reduced to a  
13   target value during a dewaxing step, using catalytic or solvent dewaxing. In  
14   conventional processes, the viscosity index generally decreases during  
15   dewaxing, since conventional dewaxing processes remove high viscosity  
16   index wax from the lubricating oil base stock. Improvements in automotive  
17   engine design is putting ever increasing pressure on the quality of motor oils.  
18   Demand for low volatility oils having superior low temperature properties is  
19   increasing, and refiners are constantly looking for new processes to aid them  
20   in meeting current demands.

21           High quality lubricants should be, and generally are, paraffinic in  
22   nature, since paraffins have a high viscosity index. However, normal  
23   paraffins, in particular, are waxy in character, and contribute to a high pour  
24   point in the oil. Conventional processes for removing these normal paraffins  
25   reduce yield of the lubricant, and have a tendency to reduce the viscosity  
26   index of the dewaxed oil. The viscosity index may be increased in the  
27   lubricating oil base stock by addition of viscosity index improvers. However,  
28   viscosity index improvers are expensive, and tend to fragment at conditions of  
29   high temperature and high shear, both of which are commonly found in  
30   modern automotive engines.

1           Synthetic lubricants may be used when very low pour point and very  
2 high viscosity index lubricants are desired. But the starting materials used to  
3 make the synthetic lubricants, and the processes used in manufacturing these  
4 lubricants, are very expensive. The need remains for a lubricating oil base  
5 stock, having synthetic-like properties but prepared from a mineral oil feed  
6 using methods which are similar to those presently employed in refinery  
7 processes.

8           A major breakthrough came with the discovery of new dewaxing  
9 catalysts which were found to isomerize rather than crack the wax molecules.  
10 Isomerization alters the molecular structure of wax molecules, and generally  
11 decreases the pour point of the molecule without significantly changing its  
12 boiling point. In contrast to solvent dewaxing and to wax cracking, isomerized  
13 molecules are retained in the lubricating oil base stock, increasing yield of  
14 lubricating oil base stock without reducing viscosity index significantly. A  
15 particularly important group of isomerization catalysts include the  
16 silicoaluminophosphate molecular sieves (SAPO). The preparation of  
17 silicoaluminophosphate molecular sieves, including SAPO-11, SAPO-31 and  
18 SAPO-41, are taught, for example, in U.S. Patent No. 4,440,871. Dewaxing  
19 processes using such molecular sieves are taught in U.S. Patent  
20 No. 4,859,311; U.S. Patent No. 4,867,862; U.S. Patent No. 4,921,594; U.S.  
21 Patent No. 5,082,986; U.S. Patent No. 5,135,638; U.S. Patent No. 5,149,421;  
22 U.S. Patent No. 5,246,566; U.S. Patent No. 5,413,695; and U.S. Patent  
23 No. 4,960,504.

24           SAPO molecular sieves belong to an important class of non-zeolitic  
25 molecular sieve dewaxing catalysts which are useful as isomerization  
26 catalysts for converting wax and wax-like components. Non-zeolitic molecular  
27 sieves are microporous compositions that are formed from  $\text{AlO}_2$  and  $\text{PO}_2$   
28 tetrahedra which form 3-dimensional crystalline structures, and are described  
29 broadly for this use in U.S. Patent No. 4,906,351 and U.S. Patent  
30 No. 4,880,760.

1           These catalysts with isomerization and hydroisomerization activity have  
2   been found to provide a method for preparing very high viscosity index  
3   lubricating oil base stocks from waxy feedstocks in a single reaction step.  
4   Producing a C<sub>20</sub><sup>+</sup> lube oil from olefins, including normal alpha olefins, using an  
5   intermediate pore size molecular sieve and at least one Group VIII metal, is  
6   taught in U.S. Patent No. 5,082,986. In U.S. Patent No. 5,135,638, a waxy  
7   feed containing greater than about 50% wax is isomerized over a catalyst  
8   comprising a molecular sieve having 1-D pores having a minor axis between  
9   about 4.2Å and about 4.8Å and a major axis between about 5.4Å and about  
10   7.0Å and at least one Group VIII metal at a pressure of from about 15 psig  
11   (103 kPa) to about 2000 psig (13.8 MPa). SAPO-11, SAPO-31, SAPO-41,  
12   ZSM-22, ZSM-23 and ZSM-35 are included in U.S. Patent No. 5,135,638 as  
13   intermediate pore size materials which possess the indicated pore geometry.  
14   In U.S. Patent No. 5,282,958, a feed including straight chain and slightly  
15   branched chain paraffins having 10 or more carbon atoms is isomerized with  
16   an intermediate pore size molecular sieve having a defined pore geometry,  
17   crystallite size, acidity and isomerization selectivity. Feeds which may be  
18   processed by the method of U.S. Patent No. 5,282,958 include waxy feeds,  
19   which contain greater than about 50% wax. Such feeds are also taught as  
20   often containing greater than 70% paraffinic carbon. U.S. Patent  
21   No. 5,376,260 is directed to pour point reduction of a heavy oil which contains  
22   naphthenic wax, using SSZ-32. Heavy oils comprising up to 100% wax are  
23   taught.

24           Large pore zeolites represent another class of catalysts which have  
25   been taught for wax isomerization. EP 464546 teaches producing a high  
26   viscosity index lubricant from a petroleum wax feed having a paraffin content  
27   of at least 40 weight percent. The catalyst is a low acidity zeolite  
28   isomerization catalyst having an alpha value of not more than 20. Zeolite  
29   beta which contains boron as a framework component of the zeolite is taught  
30   as being preferred. The catalyst in WO 96/26993 is a low acidity large pore  
31   zeolite isomerization catalyst having a ratio of SiO<sub>2</sub>/Al<sub>2</sub>O<sub>3</sub>, as synthesized, of

1 at least 200:1. WO 96/13563 teaches an isomerization process for producing  
2 a high viscosity index lubricant using a low acidity large pore molecular sieve  
3 having a crystal size of less than 0.1 micron, an alpha value of not more than  
4 30 and containing a noble metal hydrogenation component. EP 225053  
5 teaches isomerization dewaxing using a large pore, high silica zeolite  
6 dewaxing catalyst, followed by a subsequent dewaxing step which selectively  
7 removes the more waxy n-paraffin components. The selective dewaxing step  
8 may be either a solvent or a catalyst dewaxing, preferably using highly shape  
9 selective zeolite such as ZSM-22 or ZSM-23.

10 While the intermediate pore size molecular sieves have been shown to  
11 be effective for producing high viscosity index lubricating oil base stocks, the  
12 need remains for even higher viscosity index products which have been  
13 dewaxed to a low pour point.

#### 14 SUMMARY OF THE INVENTION

15 An object of the present invention is to provide a process for producing an oil,  
16 having a very high viscosity index and a very low pour point, which is suitable  
17 for use as a lubricating oil base stock. The feedstock to the present process  
18 is a waxy feed which may be derived from mineral oils and mineral oil crudes.  
19 The oil which is produced has lubricating oil properties that approach, and  
20 may exceed, the lubricating oil properties of a synthetic lubricating oil base  
21 stock. Accordingly, the present invention provides a process for preparing an  
22 oil suitable for use as a lubricating oil base stock and having a viscosity index  
23 of greater than 140 and a target pour point of less than or equal to  $-10^{\circ}\text{C}$   
24 comprising:

- 25 a) contacting a waxy feed over a catalyst comprising a molecular sieve  
26 having 1-D pores with a pore diameter of between about 5.0 Å and  
27 about 7.0 Å, and at least one Group VIII metal, at a pressure of from  
28 about 15 psig (103 kPa) to about 2500 psig (13.8 MPa) to produce an  
29 isomerized oil having a pour point of at least  $6^{\circ}\text{C}$  above a target pour  
30 point; and

1       b) solvent dewaxing the isomerized oil to produce a lubricating oil base  
2       stock having the target pour point and a viscosity index of greater than  
3       about 140.

4 A particularly preferred molecular sieve useful in the isomerization step  
5 has sufficient isomerization selectivity such that, when contacting a n-C<sub>24</sub> feed  
6 at a total pressure of 1000 psig (6.99 MPa), hydrogen flow equivalent to 6.7  
7 MSCF/bbl (1010 std liters H<sub>2</sub>/kg oil), and a feed rate equivalent to 0.6 hr<sup>-1</sup>  
8 LHSV with a catalyst comprising the molecular sieve, to produce a 316°C+  
9 dewaxed product having a pour point of about +20°C and solvent dewaxing  
10 the dewaxed product to a pour point of -15°C or below, an isomerized  
11 product having a branching index of less than about 1.75 is formed.

12 The process is capable of producing an oil having a very high viscosity  
13 index, e.g., greater than about 140 or even greater than about 150. The  
14 process is further capable of producing an oil having a very low pour point,  
15 e.g. less than or equal to about -10°C, or less than or equal to about -20°C, or  
16 even less than or equal to about -30°C.

17 In another embodiment, the present invention provides a unique  
18 lubricating oil base stock, which has a viscosity index of at least about 140,  
19 preferably at least about 150 and more preferably at least about 160, a pour  
20 point of less than or equal to about -10°C, and a viscosity, measured at  
21 100°C, of about 3 cSt or less.

22 IN THE FIGURES

Figure 1 shows the benefit of isomerizing a waxy feed with SM-3 and solvent dewaxing the isomerized oil compared to isomerizing the waxy feed alone.

Figure 2 shows the benefit of isomerizing a waxy feed with SSZ-32 and solvent dewaxing the isomerized oil compared to isomerizing the waxy feed alone.

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### DETAILED DESCRIPTION OF THE INVENTION

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Normal paraffins are a major contributor to wax and a high pour point in a lubricating oil base stock. It is desirable to isomerize the normal paraffins to low pour point branched paraffins which retain the boiling range of the normal paraffins from which there were converted.

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Among other factors, the present invention is based on the discovery that the number of branches produced while isomerizing a normal paraffin molecule significantly impacts the quality of the dewaxed oil product. For example, isomerizing a normal C<sub>24</sub> paraffin, tetracosane, using a large pore zeolite catalyst conventionally taught for wax isomerization, generally produces a significant quantity of triply branched paraffin isomers. Even medium pore catalysts taught for wax isomerization, when isomerizing a waxy feed to a low pour point, produces significant quantities of the triply branched isomers. While not wishing to be bound by theory, it is believed that normal paraffins are first converted during wax isomerization to a singly branched paraffin having a methyl (—CH<sub>3</sub>) or ethyl (—C<sub>2</sub>H<sub>5</sub>), branch near the end of the paraffin backbone. Additional isomerization reactions move the branch toward the center of the paraffin molecule and/or add a second branch to the paraffin molecule. Each of these two isomerization reaction steps reduces pour point.

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However, conventional single stage and/or large pore zeolite dewaxing processes are unselective for forming branches. These unselective catalysts produce triply (or even more highly) branched isomers along with the singly and doubly branched isomers before reaching the target pour point. These highly branched molecules have an increased tendency to crack and have a lower viscosity index than do singly or doubly branched paraffins. Furthermore, the addition of a third branch to a doubly branched paraffin often results in relatively little additional pour point reduction. Thus, these conventional processes are prevented from producing lubes with the desired viscosity index and pour point properties.

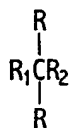


1 In the present process, normal paraffins are isomerized at high  
 2 selectivity to singly and doubly branched paraffins using a process which  
 3 produces few triply branched paraffins. The shape selective catalyst of the  
 4 present invention, comprising a 1-D intermediate pore size molecular sieve,  
 5 restricts the amount of triply branched paraffins which are formed in the  
 6 isomerization of a waxy feed, while producing a product having an  
 7 intermediate pour point. The remaining wax is removed in a solvent dewaxing  
 8 step to produce a lubricating oil base stock with a very low pour point and a  
 9 viscosity index which approaches, and can exceed, the viscosity index of  
 10 synthetic lubricants having the same viscosity.

11 As used herein, a normal paraffin, or alkane, is a saturated aliphatic  
 12 hydrocarbon containing only  $-\text{CH}_3$  and  $-\text{CH}_2-$  groups. A branched paraffin is  
 13 a saturated aliphatic hydrocarbon containing one or more



or



14 groups. As used herein, each R represents a branch, where R is an alkyl  
 15 independently selected from  $-\text{CH}_3$ ,  $-\text{C}_2\text{H}_5$ ,  $-\text{C}_3\text{H}_7$ , or  $-\text{C}_4\text{H}_9$ , and preferably  
 16 from  $-\text{CH}_3$  or  $-\text{C}_2\text{H}_5$ .  $\text{R}_1$  and  $\text{R}_2$  represent portions of the paraffin chain or  
 17 backbone. Thus, a singly branched paraffin has one R group per paraffin  
 18 molecule, a doubly branched paraffin two R groups, a triply branched paraffin  
 19 three R groups, etc.

20 The feedstock to the present process is a "waxy feed". The feedstock  
 21 will normally be a  $\text{C}_{20}^+$  feedstock, generally boiling above about  $316^\circ\text{C}$  and  
 22 containing paraffins, olefins, naphthenes, aromatics and heterocyclic  
 23 compounds and a substantial proportion of higher molecular weight

1 n-paraffins and slightly branched paraffins which contribute to the waxy  
2 nature of the feedstock. Hydroprocessed stocks are a convenient source of  
3 stocks of this kind and also of other distillate fractions since they normally  
4 contain significant amounts of waxy n-paraffins.

5 As used herein, the term "waxy feed" includes petroleum waxes.  
6 Exemplary suitable feeds for use in the process of the invention also include  
7 waxy distillate stocks such as gas oils, lubricating oil stocks, synthetic oils and  
8 waxes such as those by Fischer-Tropsch synthesis, high pour point  
9 polyalphaolefins, foots oils, normal alpha olefin waxes, slack waxes, deoiled  
10 waxes and microcrystalline waxes. Slack wax is wax recovered from a  
11 conventional solvent dewaxing process. Slack wax can be obtained from  
12 either a straight run gas oil, a hydrocracked lube oil or a solvent refined lube  
13 oil. Hydrocracking is preferred because that process can also reduce the  
14 nitrogen content to low values. With slack wax derived from solvent refined  
15 oils, deoiling can be used to reduce the nitrogen content. Optionally,  
16 hydrotreating of the slack wax can be carried out to lower the nitrogen content  
17 thereof. Slack waxes possess a very high viscosity index, normally in the  
18 range of from 120 to 200, depending on the oil content and the starting  
19 material from which the wax has been prepared. Slack waxes are therefore  
20 eminently suitable for the preparation of lubricating oils having very high  
21 viscosity indices, i.e., from about 140 to about 180. Foots oil is prepared by  
22 separating oil from the wax. The isolated oil is referred to as foots oil.

23 The feedstock employed in the process of the invention preferably  
24 contains greater than about 50% wax, more preferably greater than about  
25 80% wax, most preferably greater than about 90% wax. However, a highly  
26 paraffinic feed having a high pour point, generally above about 0°C, more  
27 usually above about 10°C, but containing less than 50% wax is also suitable  
28 for use in the process of the invention. Such a feed should preferably contain  
29 greater than about 70% paraffinic carbon, more preferably greater than about  
30 80% paraffinic carbon, most preferably greater than about 90% paraffinic  
31 carbon.

1           A catalyst useful in the present process comprises an intermediate  
2 pore size molecular size and a hydrogenation component. Catalysts of this  
3 type are taught in U.S. Patent No. 5,135,638, the entire disclosure of which is  
4 incorporated herein by reference for all purposes. The phrase "intermediate  
5 pore size", as used herein means an effective pore aperture in the range of  
6 from about 5.0 to about 7.0 Å, preferably from about 5.3 to about 6.5Å, when  
7 the porous inorganic oxide is in the calcined form. The effective pore size of  
8 the molecular sieves can be measured using standard adsorption techniques  
9 and hydrocarbonaceous compounds of known minimum kinetic diameters.  
10 See Breck, Zeolite Molecular Sieves. 1974 (especially Chapter 8); Anderson  
11 et al., J. Catalysis 58, 114 (1979); and U.S. Pat. No. 4,440,871, the pertinent  
12 portions of which are incorporated herein by reference.

13           In performing adsorption measurements to determine pore size,  
14 standard techniques are used. It is convenient to consider a particular  
15 molecule as excluded if it does not reach at least 95% of its equilibrium  
16 adsorption value on the molecular sieve in less than about 10 minutes  
17 ( $p/p_o=0.5$ ; 25°C).

18           Intermediate pore size molecular sieves will typically admit molecules  
19 having kinetic diameters of 5.3 to 6.5Å with little hindrance. Examples of such  
20 compounds (and their kinetic diameters in Å) are: n-hexane (4.3),  
21 3-methylpentane (5.5), benzene (5.85), and toluene (5.8). Compounds  
22 having kinetic diameters of about 6 to 6.5Å can be admitted into the pores,  
23 depending on the particular sieve, but do not penetrate as quickly and in  
24 some cases are effectively excluded. Compounds having kinetic diameters in  
25 the range of 6 to 6.5Å include: cyclohexane (6.0), 2,3-dimethylbutane (6.1),  
26 and m-xylene (6.1). Generally, compounds having kinetic diameters of  
27 greater than about 6.5Å do not penetrate the pore apertures and thus are not  
28 absorbed into the interior of the molecular sieve lattice. Examples of such  
29 larger compounds include: o-xylene (6.8), 1,3,5-trimethylbenzene (7.5), and  
30 tributylamine (8.1). While the effective pore size as discussed above is  
31 important to the practice of the invention, not all intermediate pore size

1 molecular sieves having such effective pore sizes are advantageously usable  
2 in the practice of the present invention. Indeed, it is essential that the  
3 intermediate pore size molecular sieve catalysts used in the practice of the  
4 present invention have a very specific pore shape and size as measured by  
5 X-ray crystallography. First, the intracrystalline channels must be parallel and  
6 must not be interconnected. Such channels are conventionally referred to as  
7 1-D diffusion types or more shortly as 1-D pores. The classification of  
8 intrazeolite channels as 1-D, 2-D and 3-D is set forth by R. M. Barrer in  
9 Zeolites, Science and Technology, edited by F. R. Rodrigues, L. D. Rollman  
10 and C. Naccache, NATO ASI Series, 1984 which classification is  
11 incorporated in its entirety by reference (see particularly page 75). Known  
12 1-D zeolites include cancrinite hydrate, laumontite, mazzite, mordenite and  
13 zeolite L.

14 In general, the pores of the molecular sieve have a major axis between  
15 about 5.0 Å and about 7.0 Å, i.e. the pore diameter of the molecular sieve is  
16 between about 5.0 Å and about 7.0 Å. In one embodiment, the preferred  
17 molecular sieves useful in the practice of the present invention have pores  
18 which are oval in shape, by which is meant the pores exhibit two unequal  
19 axes referred to herein as a minor axis and a major axis. The term oval as  
20 used herein is not meant to require a specific oval or elliptical shape but  
21 rather to refer to the pores exhibiting two unequal axes. In particular, the 1-D  
22 pores of the preferred molecular sieves useful in the practice of the present  
23 invention have a minor axis between about 3.9Å and about 4.8Å and a major  
24 axis between about 5.4Å and about 7.0Å as determined by conventional  
25 X-ray crystallography measurements, following the measurement convention  
26 of W. M. Meier and D. H. Olson, *ATLAS OF ZEOLITE STRUCTURE TYPES*,  
27 Butterworth-Heinemann, Third Revised Edition, 1992.

28 The present invention makes use of molecular sieve catalysts with  
29 selected shape selectivity properties. These shape selectivity properties are  
30 defined by carrying out standard isomerization selectivity tests for isomerizing  
31 tetracosane (n-C<sub>24</sub>). The test conditions include a total pressure of 1000 psig

1 (6.89 MPa), hydrogen flow equivalent to 6.7 MSCF/bbl (1010 std liters H<sub>2</sub>/kg  
2 oil), a feed rate equivalent to 0.6 hr<sup>-1</sup>·LHSV and the use of 0.5g of catalyst  
3 (impregnated with 0.5 wt% Pt and sized to 24-42 mesh [0.35 mm – 0.70 mm])  
4 loaded in the center of a 3 feet long (0.91 m) by 3/16 inch (0.48 cm) inner  
5 diameter stainless steel reactor tube (the catalyst is located centrally of the  
6 tube and extends about 1 to 2 inches [2.54-5.08 cm] in length) with alundum  
7 loaded upstream of the catalyst for preheating the feed. The reactor  
8 temperature is adjusted to achieve a pour point of about +20°C in the 600°F+  
9 (316°C) distillation bottoms of the reactor effluent. The 600°F+ (316°C)  
10 distillation bottoms are then solvent dewaxed to a pour point of about -15°C.

11 To account for the extent of isomerization, a branching index is defined  
12 to characterize the average number of branches per C<sub>24</sub> molecule.

13 
$$BranchingIndex = \sum_i i * b_i / b_t$$

14 where b<sub>i</sub> is the amount of paraffins in the product with an "i" number of  
15 branches, and b<sub>t</sub> is the total amount of paraffins in the product (both normal  
16 and branched).

17 The branching index is determined by analyzing a sample of the  
18 product from the standard isomerization selectivity test using carbon-13 NMR  
19 according to the following four-step process. References cited in the  
20 description detail the process steps.

- 21 1. Identify the CH branch centers and the CH<sub>3</sub> branch termination points  
22 using the DEPT Pulse sequence (Doddrell, D.T.; Pegg, D. T.; Bendall,  
23 M.R. *J. Magn. Reson.* **1982**, 48, 323ff.).
- 24 2. Verify the absence of carbons initiating multiple branches (quaternary  
25 carbons) using the APT pulse sequence (Patt, S.L.; Shoolery, J. N. *J.*  
26 *Magn. Reson.* **1982**, 46, 535ff.)
- 27 3. Assign the various branch carbon resonances to specific branch  
28 positions and lengths using tabulated and calculated values

1 (Lindeman, L. P.; Adams, J. Q. *Anal. Chem.* **43**, 1971 1245ff; Netzel,  
2 D.A. *et.al. Fuel*, **60**, 1981, 307ff.

3 4. Quantify the relative frequency of branch occurrence by comparing the  
4 integrated intensity of its terminal methyl carbon to the intensity of a  
5 single carbon (=total integral/number of carbons per molecule in the  
6 mixture). For the unique case of the isopropyl branch, where both  
7 methyl occur at the same resonance position, the intensity was divided  
8 by two before doing the frequency of branch occurrence calculation.

9 All measurements were performed with Varian 300 MHz spectrometers.  
10 In all cases the spectral width was limited to the saturated carbon region,  
11 about 0-80 ppm vs. TMS (tetramethyl silane). 15-25% solutions by weight in  
12 chloroform-d1 excited by 45° pulses followed by an 0.8 sec acquisition time.  
13 In order to minimize non uniform intensity data, the proton decoupler was  
14 gated off during a 10 sec delay prior to the excitation pulse and on during  
15 acquisition. Total experiment times ranged from 11-80 minutes. The DEPT  
16 and APT sequences were carried out according to literature descriptions with  
17 minor deviations described in the Varian operating manuals.

18 A catalyst, if it is to qualify as a catalyst of this invention, when tested in  
19 this manner, must convert sufficient normal C<sub>24</sub> paraffin to form an isomerized  
20 product having a pour point of about -15°C or less and a branching index of  
21 less than about 1.75. Non-zeolitic molecular sieves having the characteristics  
22 of an intermediate pore size molecular sieve as described herein are useful in  
23 the present process. Non-zeolitic molecular sieves are microporous  
24 compositions that are formed from AlO<sub>2</sub> and PO<sub>2</sub> tetrahedra. Thus, the  
25 process of the invention may be carried out using a catalyst comprising an  
26 intermediate pore size non-zeolitic molecular sieve and at least one  
27 Group VIII metal. Non-zeolitic molecular sieves are described, for example,  
28 in U.S. Patent No. 4,861,743, the disclosure of which is completely  
29 incorporated herein by reference for all purposes. Non-zeolitic molecular  
30 sieves include aluminophosphates (AlPO<sub>4</sub>) as described in U.S. Patent  
31 No. 4,310,440, silicoaluminophosphates (SAPO), metalloaluminophosphates

1 (MeAPO), and nonmetal substituted aluminophosphates (ElAPO).  
2 Metalloaluminophosphate molecular sieves are described in U.S. Patent  
3 Nos. 4,500,651; 4,567,029; 4,544,143; 4,686,093 and 4,861,743. Nonmetal  
4 substituted aluminophosphates are described in U.S. Patent No. 4,973,785.

5 Methods for forming a non-zeolitic molecular sieves may be found, for  
6 example, in U.S. Patent Nos. 4,440,871; 4,710,485; and 4,973,785. Non-  
7 zeolitic molecular sieves are generally synthesized by hydrothermal  
8 crystallization from a reaction mixture comprising reactive sources of  
9 aluminum, phosphorus, optionally one or more elements, other than  
10 aluminum and phosphorous, which are capable of forming oxides in  
11 tetrahedral coordination with  $\text{AlO}_2$  and  $\text{PO}_2$  units, and one or more organic  
12 templating agents. The reaction mixture is placed in a sealed pressure vessel  
13 and heated, preferably under autogenous pressure at a temperature of at  
14 least about  $100^\circ\text{C}$ ., and preferably between  $100^\circ\text{C}$ . and  $250^\circ\text{C}$ ., until crystals  
15 of the molecular sieve product are obtained, usually for a period of from 2  
16 hours to 2 weeks.

17 A silicoaluminophosphate molecular sieve is suitable as an  
18 intermediate pore size molecular sieve for the present process. The  
19 silicoaluminophosphate molecular sieves belong to a class of non-zeolitic  
20 molecular sieves characterized by a three-dimensional microporous  
21 framework structure of  $\text{AlO}_2$ , and  $\text{PO}_2$  tetrahedral oxide units with a unit  
22 empirical formula on an anhydrous basis of:



24 wherein "x", "y", and "z" represent the mole fractions, respectively, of silicon,  
25 aluminum, and phosphorus, wherein "x" has a value equal to or greater than  
26 zero (0), and "y" and "z" each have a value of at least 0.01.

27 Catalytic particulates containing at least one of the intermediate pore  
28 molecular sieves SAPO-11, SAPO-31 and SAPO-41 are particularly useful in  
29 the present process. U.S. Patent No. 4,440,871 describes SAPO's generally  
30 and SAPO-11, SAPO-31, and SAPO-41 specifically. The most preferred

1 intermediate pore size silicoaluminophosphate molecular sieve for use in the  
 2 process of the invention is SAPO-11. When combined with a platinum or  
 3 palladium hydrogenation component, the SAPO-11 converts the waxy  
 4 components to produce a lubricating oil having excellent yield, very low pour  
 5 point, low viscosity and high viscosity index.

6 SAPO-11 comprises a silicoaluminophosphate material having a  
 7 three-dimensional microporous crystal framework structure of  $\text{PO}_2$ ,  $\text{AlO}_2$  and  
 8  $\text{SiO}_2$  tetrahedral units whose unit empirical formula on an anhydrous basis is:



10 wherein "R" represents at least one organic templating agent present in the  
 11 intracrystalline pore system; "m" represents the moles of "R" present per mole  
 12 of  $(\text{Si}_x\text{Al}_y\text{P}_z)\text{O}_2$  and has a value of from zero to about 0.3, "x", "y" and "z"  
 13 represent respectively, the mole fractions of silicon, aluminum and  
 14 phosphorous, wherein "x" has a value greater than zero (0), and "y" and "z"  
 15 each have a value of at least 0.01. The silicoaluminophosphate has a  
 16 characteristic X-ray powder diffraction pattern which contains at least the  
 17 d-spacings (as-synthesized and calcined) set forth below in Table I. When  
 18 SAPO-11 is in the as-synthesized form, "m" preferably has a value of from  
 19 0.02 to 0.3.

20

21

22

TABLE I			
	<u><math>2\Theta</math></u>	<u>Interplanar d-spacings (Å)</u>	<u>Relative Intensity, I/I<sub>0</sub></u>
23	9.4-9.65	9.41-9.17	m
24	20.3-20.6	4.37-4.31	m
25	21.0-21.3	4.23-4.17	vs
26	22.1-22.35	4.02-3.99	m
27	22.5-22.9 (doublet)	3.95-3.92	m-s

28 The most particularly preferred intermediate pore SAPO prepared by  
 29 the present process is SM-3, which has a crystalline structure falling within  
 30 that of the SAPO-11 molecular sieves. The preparation of SM-3 and its  
 31 unique characteristics are described in U.S. Patent Nos. 4,943,424 and



1 5,158,665. The entire disclosure of each of these patents is incorporated  
2 herein by reference for all purposes.

3 Another intermediate pore size silicoaluminophosphate molecular  
4 sieve preferably used in the process of the invention is SAPO-31. SAPO-31  
5 comprises a silicoaluminophosphate having a three-dimensional microporous  
6 crystal framework of  $\text{PO}_2$ ,  $\text{AlO}_2$  and  $\text{SiO}_2$  tetrahedral units whose unit  
7 empirical formula on an anhydrous basis is:



9 wherein R represents at least one organic templating agent present in the  
10 intracrystalline pore system; "m" represents the moles of "R" present per mole  
11 of  $(\text{Si}_x\text{Al}_y\text{P}_z)\text{O}_2$  and has a value of from zero to 0.3; "x", "y" and "z" represent,  
12 respectively, the mole fractions of silicon, aluminum and phosphorous,  
13 wherein "x" has a value greater than zero (0), and "y" and "z" each have a  
14 value of at least 0.01. The silicoaluminophosphate has a characteristic X-ray  
15 powder diffraction pattern (as-synthesized and calcined) which contains at  
16 least the d-spacings set forth below in Table II. When SAPO-31 is in the  
17 as-synthesized form, "m" preferably has a value of from 0.02 to 0.3.

18 TABLE II

19	20	21	22	23	24	25	26
		<u>2<math>\theta</math></u>	<u>Interplanar</u>	<u>d-spacings (Å)</u>	<u>Relative</u>		
		8.5-8.6	10.40-10.28	m-s			
		20.2-20.3	4.40-4.37	m			
		21.9-22.1	4.06-4.02	w-m			
		22.6-22.7	3.93-3.92	vs			
		31.7-31.8	3.823-2.814	w-m			

27 SAPO-41, also suitable for use in the process of the invention,  
28 comprises a silicoaluminophosphate having a three-dimensional microporous  
29 crystal framework structure of  $\text{PO}_2$ ,  $\text{AlO}_2$  and  $\text{SiO}_2$  tetrahedral units, and  
30 whose unit empirical formula on an anhydrous basis is:



32 wherein R represents at least one organic templating agent present in the  
33 intracrystalline pore system; "m" represents the moles of "R" present per mole

1 of  $(\text{Si}_x\text{Al}_y\text{P}_z)\text{O}_2$  and has a value of from zero to 0.3; "x", "y" and "z" represent,  
 2 respectively, the mole fractions of silicon, aluminum and phosphorous,  
 3 wherein "x" has a value greater than zero (0), and "y" and "z" each have a  
 4 value of at least 0.01. SAPO-41 has characteristic X-ray powder diffraction  
 5 pattern (as-synthesized and calcined) which contains at least the d-spacings  
 6 set forth below in Table III. When SAPO-41 is in the as-synthesized form,  
 7 "m" preferably has a value of from 0.02 to 0.03.

TABLE III

9	2 $\theta$	Interplanar d-spacings (Å)	Relative Intensity, I/I <sub>o</sub>
10			
11	13.6-13.8	6.51-6.42	w-m
12	20.5-20.6	4.33-4.31	w-m
13	21.1-21.3	4.21-4.17	vs
14	22.1-22.3	4.02-3.99	m-s
15	22.8-23.0	3.90-3.86	m
16	23.1-23.4	3.82-3.80	w-m
17	25.5-25.9	3.493-3.44	w-m

18 The group of intermediate pore size zeolites useful in the present  
 19 process include ZSM-22, ZSM-23, ZSM-35, ZSM-48 and SSZ-32. These  
 20 catalysts are generally considered to be intermediate pore size catalysts  
 21 based on the measure of their internal structure as represented by their  
 22 Constraint Index. Zeolites which provide highly restricted access to and  
 23 egress from their internal structure have a high value for the Constraint Index,  
 24 while zeolites which provide relatively free access to the internal zeolite  
 25 structure have a low value for their Constraint Index. The method for  
 26 determining Constraint Index is described fully in U.S. Pat. No. 4,016,218  
 27 which is incorporated herein by reference.

28 One of the zeolites of the present invention, ZSM-22, is a highly  
 29 siliceous material which includes crystalline three-dimensional continuous  
 30 framework silicon containing structures or crystals which result when all the  
 31 oxygen atoms in the tetrahedra are mutually shared between tetrahedral

atoms of silicon or aluminum, and which can exist with a network of mostly SiO<sub>2</sub>, i.e., exclusive of any intracrystalline cations. The description of ZSM-22 is set forth in full in U.S. Pat. No. 4,556,477, U.S. Pat. No. 4,481,177 and European Patent Application No. 102,716 the contents of which are incorporated herein by reference.

As indicated in U.S. Pat. No. 4,566,477, the crystalline material ZSM-22 has been designated with a characteristic X-ray diffraction pattern as set forth in Table IV.

TABLE IV  
Most Significant Lines of ZSM-22

	Interplanar d-spacings (Å)	Relative Intensity (I/I <sub>0</sub> )
	10.9 ± 0.2	m-vs
	8.7 ± 0.16	w
	6.94 ± 0.10	w-m
	5.40 ± 0.08	w
	4.58 ± 0.07	w
	4.36 ± 0.07	vs
	3.68 ± 0.05	vs
	3.62 ± 0.05	s-vs
	3.47 ± 0.04	m-s
	3.30 ± 0.04	w
	2.74 ± 0.02	w
	2.52 ± 0.02	w

It should be understood that the X-ray diffraction pattern of Table VII is characteristic of all the species of ZSM-22 zeolite compositions. Ion exchange of the alkali metal cations with other ions results in a zeolite which reveals substantially the same X-ray diffraction pattern with some minor shifts in interplanar spacing and variation in relative intensity.

Furthermore, the original cations of the as-synthesized ZSM-22 can be replaced at least in part by other ions using conventional ion exchange techniques. It may be necessary to pre-calcine the ZSM-22 zeolite crystals prior to ion exchange. In accordance with the present invention, the

1 replacement ions are those taken from Group VIII of the Periodic Table,  
 2 especially platinum, palladium, iridium, osmium, rhodium and ruthenium.

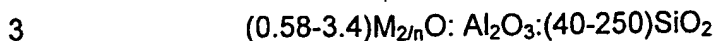
3 ZSM-22 freely sorbs normal hexane and has a pore dimension greater  
 4 than about 4Å. In addition, the structure of the zeolite provides constrained  
 5 access to larger molecules. The Constraint Index as determined by the  
 6 procedure set forth in U.S. Pat. No. 4,016,246 for ZSM-22 has been  
 7 determined to be from about 2.5 to about 3.0.

8 Another zeolite which can be used with the present invention is the  
 9 synthetic crystalline aluminosilicate referred to as ZSM-23, disclosed in U.S.  
 10 Pat. No. 4,076,842, the contents of which are incorporated herein by  
 11 reference. The ZSM-23 composition has a characteristic X-ray diffraction  
 12 pattern as set forth herein in Table V.

TABLE V

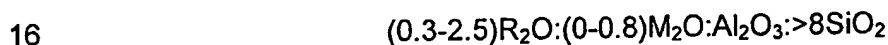
14	Interplanar	Relative
15	<u>d-spacings (Å)</u>	<u>Intensity, I/I<sub>0</sub></u>
16	11.2 ±0.23	m
17	10.1 ±0.20	w
18	7.87 ±0.15	w
19	5.59 ±0.10	w
20	5.44 ±0.10	w
21	4.90 ±0.10	w
22	4.53 ±0.10	s
23	3.90 ±0.08	vs
24	3.72 ±0.08	vs
25	3.62 ±0.07	vs
26	3.54 ±0.07	m
27	3.44 ±0.07	s
28	3.36 ±0.07	w
29	3.16 ±0.07	w
30	3.05 ±0.06	w
31	2.99 ±0.06	w
32	2.85 ±0.06	w
33	2.54 ±0.05	m
34	2.47 ±0.05	w
35	2.40 ±0.05	w
36	2.34 ±0.05	w
37		

1 The ZSM-23 composition can also be defined in terms of mole ratios of  
2 oxides in the anhydrous state as follows:



4 wherein M is at least 1 cation and n is the valence thereof. As in the ZSM-22,  
5 the original cations of as-synthesized ZSM-23 can be replaced in accordance  
6 with techniques well-known in the art, at least in part by ionic exchange with  
7 other cations. In the present invention these cations include the Group VIII  
8 metals as set forth hereinbefore.

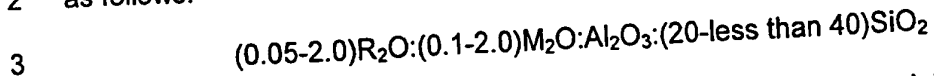
9 Another intermediate pore size zeolite which has been found to be  
10 successful in the present invention is ZSM-35, which is disclosed in U.S.  
11 Patent No. 4,016,245, the contents of which are incorporated herein by  
12 reference. The synthetic crystalline aluminosilicate known as ZSM-35, has a  
13 characteristic X-ray diffraction pattern which is set forth in U.S. Pat.  
14 No. 4,016,245. ZSM-35 has a composition which can be defined in terms of  
15 mole ratio of oxides in the anhydrous state as follows:



17 wherein R is organic nitrogen-containing cation derived from ethylenediamine  
18 or pyrrolidine and M is an alkali metal cation. The original cations of the  
19 as-synthesized ZSM-35 can be removed using techniques well known in the  
20 art which includes ion exchange with other cations. In the present invention,  
21 the cation exchange is used to replace the as-synthesized cations with the  
22 Group VIII metals set forth herein. It has been observed that the X-ray  
23 diffraction pattern of ZSM-35 is similar to that of natural ferrierite with a  
24 notable exception being that natural ferrierite patterns exhibit a significant line  
25 at 1.33Å.

26 Another intermediate pore size zeolite which has been found to be  
27 successful in the present invention is SSZ-32, which is disclosed in U.S.  
28 Patent No. 5,053,373, the content of which are incorporated herein by  
29 reference. SSZ-32 has a characteristic X-ray diffraction pattern which is set  
30 forth in U.S. Patent No. 5,053,373. The composition of SSZ-32, as

1 synthesized and in the anhydrous state, in terms of mole ratios of oxides, is  
 2 as follows:



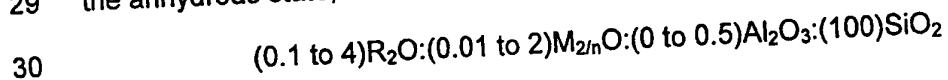
4 where M is an alkali metal cation and R is an organic nitrogen-containing  
 5 cation, such as an N-lower alkyl-N'-isopropyl-imidazolium cation. SSZ-32  
 6 has a mole ratio of silicon oxide to aluminum oxide in the range of 20 to less  
 7 than 40, and has essentially the same X-ray diffraction pattern of ZSM-23.  
 8 Hydroconversion processes using SSZ-32 are disclosed, for example, in U.S.  
 9 Patent Nos. 5,300,210 and in 5,397,454.

10 ZSM-48 is a crystalline aluminosilicate zeolite which is suitable as a  
 11 dewaxing catalyst for the present invention. Zeolite ZSM-48 is disclosed in  
 12 U.S. Patent No. 4,585,747, the entire disclosure of which is incorporated  
 13 herein by reference for all purposes, and has a characteristic X-ray diffraction  
 14 pattern as set forth in Table VI.

15  
 16 Table VI

17	Interplanar	Relative
18	<u>d-spacings (Å)</u>	<u>Intensity, I/I<sub>0</sub></u>
19	11.8 ± 0.2	s
20	10.2 ± 0.2	w-m
21	7.2 ± 0.15	w
22	4.2 ± 0.08	vs
23	3.9 ± 0.08	vs
24	3.6 ± 0.06	w
25	3.1 ± 0.05	w
26	2.85 ± 0.05	w

27  
 28 Zeolite ZSM-48 can also be identified, in terms of mole ratios of oxides and in  
 29 the anhydrous state, as follows:



1 wherein M is at least one cation having a valence n and R is the cation. The  
2 cation taught in U.S. Patent No. 4,585,747 is derived from the monomeric,  
3 diquatery compound bis(N-methylpyridyl)ethylinium.

4 Other molecular sieves which can be used with the present invention  
5 include, for example, Theta-1, as described in U.S. Pat. Nos. 4,533,649 and  
6 4,836,910, both of which are incorporated in their entireties by reference,  
7 Nu-10, as described in European Patent Application 065,400 which is  
8 incorporated in its entirety by reference and SSZ-20 as described in U.S. Pat.  
9 No. 4,483,835 which is incorporated in its entirety by reference.

10 X-ray crystallography of SAPO-11, SAPO-31, SAPO-41, ZSM-22, ZSM-23  
11 and ZSM-35 shows these molecular sieves to have the following major and  
12 minor axes: SAPO-11, major 6.3Å, minor 3.9Å; (Bennett, J. M., et al, Zeolites,  
13 1, 160(87)), SAPO-31 and SAPO-41, believed to be slightly larger than  
14 SAPO-11, ZSM-22, major 5.5Å, minor 4.5Å (Kokotailo, G. T., et al, Zeolites,  
15 5, 349(85)); ZSM-23, major 5.6Å, minor 4.5Å; ZSM-35, major 5.4Å, minor  
16 4.2Å. ZSM-48 is a molecular sieve having a 10-ring structure with 1-D pores  
17 having a 5.23 Å major axis and a 5.11 Å minor axis. (Meier, W. M. and  
18 Olsen, D. H., Atlas of Zeolite Structure Types, Butterworths, 1987).

19 It is preferred that relatively small crystal size catalyst be utilized in  
20 practicing the invention. Suitably, the average crystal size is no greater than  
21 about 10 microns (i.e. micrometers), preferably no more than about 5  
22 microns, more preferably no more than about 1 micron and still more  
23 preferably no more than about 0.5 micron.

24 The physical form of the catalyst depends on the type of catalytic  
25 reactor being employed and may be in the form of a granule or powder, and is  
26 desirably compacted into a more readily usable form (e.g., larger  
27 agglomerates), usually with a silica or alumina binder for fluidized bed  
28 reaction, or pills, prills, spheres, extrudates, or other shapes of controlled size  
29 to accord adequate catalyst-reactant contact. The preferred catalyst is in the  
30 form of extrudates with a cross-sectional diameter between about  $\frac{1}{4}$  inch and  
31 about  $\frac{1}{32}$  inch. In the catalyst, the molecular sieve can be composited with

1 other material resistant to the temperatures and other conditions employed in  
2 organic conversion processes. Such matrix materials include active and  
3 inactive materials and synthetic or naturally occurring zeolites as well as  
4 inorganic materials such as clays, silica and metal oxides. Additional porous  
5 matrix materials include silica, alumina, titania, magnesia and mixtures  
6 thereof. The matrix can be in the form of a cogel. Alumina and silica-alumina  
7 matrix materials are preferred.

8 The intermediate pore size molecular sieve is used in admixture with at  
9 least one Group VIII metal. Preferably, the Group VIII metal is selected from  
10 the group consisting of at least one of platinum and palladium and optionally,  
11 other catalytically active metals such as molybdenum, nickel, vanadium,  
12 cobalt, tungsten, zinc and mixtures thereof. Most preferably, the Group VIII  
13 metal is selected from the group consisting of at least one of platinum and  
14 palladium. The amount of metal ranges from about 0.01% to about 10% by  
15 weight of the molecular sieve, preferably from about 0.1% to about 5% by  
16 weight and more preferably from about 0.2% to about 1% by weight of the  
17 molecular sieve. The techniques of introducing catalytically active metals into  
18 a molecular sieve are disclosed in the literature, and preexisting metal  
19 incorporation techniques and treatment of the molecular sieve to form an  
20 active catalyst such as ion exchange, impregnation or occlusion during sieve  
21 preparation are suitable for use in the present process. Such techniques are  
22 disclosed in U.S. Pat. Nos. 3,236,761; 3,226,339; 3,236,762; 3,620,960;  
23 3,373,109; 4,202,996; 4,440,781 and 4,710,485; and in U.S. Application  
24 Serial No. 08/728818; the entire disclosures of which are incorporated herein  
25 by reference for all purposes.

26 The term "metal" or "active metal" as used herein means one or more  
27 metals in the elemental state or in some form such as sulfide, oxide and  
28 mixtures thereof. Regardless of the state in which the metallic component  
29 actually exists, the concentrations are computed as if they existed in the  
30 elemental state.



1           The catalyst may also contain metals which reduce the number of  
2 strong acid sites on the catalyst and thereby lower the selectivity for cracking  
3 versus isomerization. Especially preferred are the Group IIA metals such as  
4 magnesium and calcium. The Group VIII metal utilized in the process of this  
5 invention can mean one or more of the metals in its elemental state or in  
6 some form such as the sulfide or oxide and mixtures thereof. As is customary  
7 in the art of catalysis, when referring to the active metal or metals, it is  
8 intended to encompass the existence of such metal in the elementary state or  
9 in some form such as the oxide or sulfide as mentioned above, and  
10 regardless of the state in which the metallic component actually exists, the  
11 concentrations are computed as if they existed in the elemental state.

12           The catalytic isomerization step of the invention may be conducted by  
13 contacting the feed with a fixed stationary bed of catalyst, with a fixed  
14 fluidized bed, or with a transport bed. A simple and therefore preferred  
15 configuration is a trickle-bed operation in which the feed is allowed to trickle  
16 through a stationary fixed bed, preferably in the presence of hydrogen.

17           The catalytic isomerization conditions employed depend on the feed  
18 used and the desired pour point. Generally, the temperature is from about  
19 200°C to about 475°C, preferably from about 250°C and to about 450°C. The  
20 pressure is typically from about 15 psig ( 103 kPa) to about 2500 psig (27.2  
21 MPa), preferably from about 50 psig (345 kPa) to about 2000 psig (13.8  
22 MPa), more preferably from about 100 psig to about 1500 psig (10.3 MPa).  
23 The liquid hourly space velocity (LHSV) is preferably from about 0.1hr<sup>-1</sup> to  
24 about 20 hr<sup>-1</sup>, more preferably from about 0.1hr<sup>-1</sup> to about 5hr<sup>-1</sup>, and most  
25 preferably from about 0.1hr<sup>-1</sup> to about 1.0 hr<sup>-1</sup>. Low pressure and low liquid  
26 hourly space velocity provide enhanced isomerization selectivity which results  
27 in more isomerization and less cracking of the feed thus producing an  
28 increased yield.

29           Hydrogen is preferably present in the reaction zone during the catalytic  
30 isomerization process. The hydrogen to feed ratio is typically from about 500  
31 to about 30,000 SCF/bbl (standard cubic feet per barrel) (76-4540 std liters

1 H<sub>2</sub>/kg oil), preferably from about 1,000 to about 10,000 SCF/bbl (151-1510 std  
2 liters H<sub>2</sub>/kg oil). Generally, hydrogen will be separated from the product and  
3 recycled to the reaction zone. Strong acidity may also be reduced by  
4 introducing nitrogen compounds, e.g., NH<sub>3</sub> or organic nitrogen compounds,  
5 into the feed; however, the total nitrogen content should be less than 50 ppm,  
6 preferably less than 10 ppm.

7 In the dewaxing process using the catalyst of the present invention, the  
8 pour point of the isomerized product is lower than the pour point of the waxy  
9 feed to the dewaxing process. For oils of commercial interest, the pour point  
10 of the oil is generally below about 10°C, and often below 0°C. While a low  
11 pour point is desired in the product from the isomerization step, excessive  
12 isomerization has a detrimental effect on product viscosity index, as  
13 described hereinbefore. The wax content of the isomerized oil is between  
14 about 1% and about 40%, preferably between about 3% and about 20%, of  
15 the wax content of the waxy feed. The isomerization step, then preferentially  
16 removes between about 60% and about 99% by weight of the wax contained  
17 in the waxy feedstock. Thus, the pour point of the isomerized product, while  
18 being substantially lower than the pour point of the feed to the isomerization  
19 process, will be at least about 6°C, and more usually at least about 12°C  
20 above the target pour point set for the finished lubricating oil base stock. The  
21 viscosity index of the isomerized product will be generally above about 140  
22 and preferably above about 150. With some products, a viscosity index of  
23 160 or above is possible.

24 The wax content of the oil set forth herein is determined from a  
25 conventional solvent dewaxing method. An example method is as follows:

26 300 g of oil is diluted 50/50 with a 4:1 mixture of methyl ethyl ketone  
27 and toluene which is cooled to -20°C in a refrigerator. The mixture is filtered  
28 through a Coors funnel at -15 °C. using Whatman No. 3 filter paper. The wax  
29 is removed from the filter and placed in a tared 2 liter flask. The solvent is  
30 removed on a hot plate and the wax weighed.

1           The present integrated two-step process comprises a catalytic  
2 isomerization step and a solvent dewaxing step. Following the isomerization  
3 of the waxy feed, the pour point of the isomerized oil will generally be at least  
4 about 6°C and preferably at least about 12°C above a target pour point of the  
5 finished oil. Continued isomerization results in unselective isomerization and  
6 the formation of increased numbers of triply branched paraffins, resulting in a  
7 reduced viscosity index. Thus, the isomerized oil is solvent dewaxed to a  
8 desired target pour point, which is determined by the particular grade of oil  
9 which is being produced. The target pour point will generally be less than or  
10 equal to about -10°C. For high quality oils, a pour point less than or equal to  
11 about -20°C or even less than or equal to about -30°C may be preferred.  
12 Depending on the dewaxing conditions and the feeds used for the dewaxing  
13 process, a viscosity index above 140 can be achieved. Lubricating oil stocks  
14 will generally boil above 230°C (450°F), more usually above 315°C (600°F).

15           Conventional solvent dewaxing processes which are commonly used in  
16 the preparation of a lubricating oil base stock are suitable for the present  
17 integrated process. Such processes include crystallization of the wax from a  
18 chilled mixture of waxy oil and a solvent such as a blended methyl ethyl  
19 ketone/toluene solvent. The slack wax and/or the foots oil recovered as the  
20 residual oil remaining in the slack wax may be recovered or recycled to the  
21 isomerization reaction zone. The isomerized oil which is the feed to the  
22 solvent dewaxing step of the present process will generally have a pour point  
23 of less than about 40°C, and a viscosity index of greater than about 125 and  
24 preferably greater than about 140, and more preferably greater than about  
25 150.

26           Feed to the isomerization process may require pretreatment before it  
27 can be satisfactorily processed in the isomerization step. The pretreatment  
28 steps remove heteroatoms such as nitrogen and sulfur which might poison  
29 the isomerization catalyst, or low viscosity index components such as  
30 aromatics and polycyclic naphthenes. A typical hydrocracking process is

1 described, for example, in U.S. Patent No. 5,158,665, the entire disclosure of  
2 which is already incorporated by reference.

3 It may further be desired to hydrofinish the dewaxed oil in a mild  
4 hydrogenation process to produce more stable lubrication oils. The  
5 hydrofinishing can be conventionally carried out in the presence of a metallic  
6 hydrogenation catalyst, for example, platinum on alumina. The hydrofinishing  
7 can be carried out at a temperature of from about 190°C to about 340°C and  
8 a pressure of from about 400 psig to about 3000 psig (2.76-20.7 MPa). A  
9 description of a typical hydrofinishing process and catalyst which is useful in  
10 the present process is taught in U.S. Patent No. 5,158,665. Hydrofinishing in  
11 this manner is also described in U.S. Pat. 3,852,207, both of which are  
12 incorporated herein by reference for all purposes.

13 The present process is suitable for preparing very high viscosity index  
14 lubricating oil base stocks having a wide range of viscosities, including base  
15 stocks having a viscosity, measured at 100°C, of 10 cSt or higher. These  
16 base oils have a viscosity index of at least about 140 (preferably at least  
17 about 150 and more preferably at least about 160), and a pour point of less  
18 than or equal to about -10°C (preferably less than or equal to about -20°C,  
19 and more preferably less than or equal to about -30°C). A particularly  
20 important base oil prepared in the present process has a viscosity, measured  
21 at 100°C, of about 3 cSt or less, preferably less than about 3 cSt, and a  
22 viscosity index of at least about 140, preferably at least about 150, and more  
23 preferably at least about 160. This relatively light oil prepared in the present  
24 process has a viscosity index higher than that produced even in synthetic oils  
25 having a viscosity, measured at 100°C, of about 3 cSt or less.

## 26 EXAMPLES

### 27 Comparative Example A

28 Tetracosane (n-C<sub>24</sub>, purchased from Aldrich), which had a pour point of  
29 +50 C and a viscosity at 100 C of about 2.5 cSt, was isomerized over SM-3  
30 impregnated with 0.5 wt% Pt. The catalyst was pelleted, then crushed to 24-

1 42 mesh for testing. The catalyst was sulfided in situ prior to testing by  
2 injecting H<sub>2</sub>S through a septum into the hydrogen line ahead of the reactor.  
3 Isomerization was carried out in a continuous feed high pressure pilot plant  
4 with once-through hydrogen gas. Run conditions were 1000 psig total  
5 pressure (6.89 MPa), 0.6 hr<sup>-1</sup>LHSV, and 6.7 MSCF/bbl H<sub>2</sub> (1010 std liters  
6 H<sub>2</sub>/kg oil) At a pour point of -25°C, the viscosity index of the 316°C+  
7 distillation bottoms was 132 (Table VII).

8 Example 1

9 Tetracosane was isomerized over the same Pt/SM-3 catalyst as in  
10 Comparative Example A, but to a pour point of +20 °C. The 316 °C+  
11 distillation bottoms were then solvent dewaxed (SDW) to a pour point of -29  
12 °C. The viscosity index of the oil was 148 (Table VII), much higher (about 18  
13 numbers) than obtained with isomerization only to the same pour point  
14 (Figure I). In addition, the isomerized and solvent dewaxed oil had a much  
15 lower average number of branches per molecule.

TABLE VII  
ISOMERIZATION OF n-C<sub>24</sub> OVER Pt/SM-3 AT  
1000 PSIG (6.99 MPa), 0.6 hr<sup>-1</sup> LHSV,  
AND 6.7 MSCF/BBL H<sub>2</sub> (1010 std liters H<sub>2</sub>/kg oil)

	<u>Comparative Example A</u>		<u>Example 1</u>
Temperature, °C	321	332	324
n-C <sub>24</sub> Conversion, wt%	99.1	99.6	95.1
Yield, Wt%			
C4-	0.5	0.9	0.2
C5-82 °C	1.9	2.3	0.5
82-177 °C	2.8	3.2	1.7
177-316°C	8.2	12.3	4.3
316 °C+	86.6	81.3	93.3
316°C+ Distillation Yield, wt%	87.4	82.2	92.1
Solvent Dewax	No	No	Yes
Oil, wt%			65.6
Wax, wt%			32.4
Pour Point Before SDW, °C			+20
316°C+ Lube Yield, wt%	86.6	81.3	61.2
316 °C+ Lube Inspections			
Pour Point, °C	-15	-25	-29
Cloud Point, °C	-1	-8	-9
Viscosity, 40 °C, cSt	8.636	8.372	8.313
100 °C, cSt	2.579	2.507	2.556
VI	137	132	148
Avg. Branches/Molecule	1.83	1.97	1.63
Simulated Distillation, LV%, °C			
St/5	277/358	294/357	304/369
30/50	368/379	368/379	374/382
50	384	384	385
70/90	388/392	388/391	388/391
95/EP	392/394	393/394	392/398

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2 Comparative Example B

3 An extrudate catalyst containing 85 wt% SM-3 sieve and 15 wt%  
4 Catapal alumina binder was impregnated with 0.4 wt% Pt and crushed to 24-  
5 42 mesh (0.35-0.70 mm). It was used to isomerize a 7.8 cSt heavy neutral  
6 slack wax (Table VIII) at 0.5 LHSV hr<sup>-1</sup>, 1000 psig (6.99 MPa), and 8  
7 MSCF/bbl H<sub>2</sub> (1210 std liters H<sub>2</sub>/kg oil). Results are given in Table IX,  
8 showing a 144 VI at a pour point of -12°C.

9 Example 2

10 Comparative Example B was repeated, except in this case, the feed  
11 was isomerized over the SM-3 catalyst to a pour point of 0°C, followed by  
12 solvent dewaxing to -18°C. The viscosity index (143, Table IX) was about the  
13 same as in the comparative example, but the pour point was lower. In  
14 addition, the cloud point was considerably lower.

15 TABLE VIII  
16 INSPECTIONS OF HEAVY NEUTRAL SLACK WAX  
17 Sulfur, ppm 7.0

18  
19 Viscosity, 100 °C, cSt 7.818

20  
21 Simulated Distillation, LV%, °C  
22 St/5 198/371  
23 30/50 392/439  
24 50 476  
25 70/90 522/594  
26 95/EP 628/696  
27

TABLE IX  
ISOMERIZATION OF HEAVY NEUTRAL SLACK WAX  
AT 0.5 hr<sup>-1</sup> LHSV, 1000 PSIG (6.99 MPa),  
AND 8 MSCF/BBL H<sub>2</sub> (1210 std liters H<sub>2</sub>/kg oil)  
OVER Pt/SM-3 CATALYST

	Comparative Example B	Example 2
Temperature, °C	349	332
343°F+ Conversion, wt%	27.4	21.9
Wax Conversion, wt%	100	84.1
Selectivity to Lube, wt%	67.4	72.6
Pour Point before SDW, °C		0
Solvent Dewax	No	Yes
Oil, wt%		86.2
Wax, wt%		13.8
650 F+ Lube Yield, wt%	67.4	61.1
Pour Point, °C	-12	-18
Cloud Point, °C	+9	-17
Viscosity, 40 °C, cSt	41.42	37.50
100 °C, cSt	7.367	6.836
VI	144	143
Simulated Distillation, LV%, °C		
St/5	193/357	226/358
30/50	378/425	377/419
50	464	456
70/90	511/585	500/579
95/EP	617/717	629/747

#### Comparative Example C

An SM-3 catalyst similar to that of Comparative Example B was used to isomerize a hydrotreated 4.5 cSt slack wax (Table X) at 0.5 hr<sup>-1</sup> LHSV, 800 psig total pressure (5.61 MPa), and 3 MSCF/bbl H<sub>2</sub> (454 std liters H<sub>2</sub>/kg oil). Results are given in Table XI, showing a 140 VI at a pour point of -7°C.



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Example 3

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Comparative Example C was repeated, except in this case, the feed was isomerized at 1100 psig (7.58 MPa) over the SM-3 catalyst to a pour point of  $-3^{\circ}\text{C}$ , followed by solvent dewaxing to  $-14^{\circ}\text{C}$ . The viscosity index (144, Table XI) was higher than in the comparative example, and the pour point was lower.

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TABLE X  
INSPECTIONS OF HYDROTREATED SLACK WAX

Density 0.84 g/cm<sup>3</sup>

Sulfur, ppm 33

Nitrogen, ppm 0.3

Pour Point,  $^{\circ}\text{C}$  +39

Viscosity, 70  $^{\circ}\text{C}$ , cSt 8.120

100  $^{\circ}\text{C}$ , cSt 4.465

Wax, wt% 58.2

Dewaxed Oil Properties

Pour Point,  $^{\circ}\text{C}$  -8

Cloud Point,  $^{\circ}\text{C}$  -8

Viscosity, 40  $^{\circ}\text{C}$ , cSt 21.82

100  $^{\circ}\text{C}$ , cSt 4.609

VI 130

TABLE XI  
ISOMERIZATION OF HYDROTREATED SLACK WAX  
AT 0.5 hr<sup>-1</sup> LHSV AND 3 MSCF/BBL H<sub>2</sub> (450 std liters H<sub>2</sub>/kg oil)  
OVER Pt/SM-3 CATALYST

	Comparative Example C	Example 3
Temperature, °C	327	327
Pressure, MPa	5.61	7.68
Conversion <371°C, wt%	28.9	23.7
Yields, Wt%		
C4-	2.2	2.0
C5-82 °C	3.8	3.3
180-371 °C	31.7	27.8
371°C+	62.8	67.3
371°C+ Yield, Wt%	62.6	66.8
Pour Point before SDW, °C		-3
Solvent Dewax	No	Yes
Oil, wt%		96
Wax, wt%		4
371°C+ Lube Yield, wt%	62.6	64
Pour Point, °C	-7	-14
Cloud Point, °C	-4	-11
Viscosity, 40 °C, cSt	22.0	21.98
100 °C, cSt	4.746	4.785
VI	140	144
Simulated Distillation, LV%, °C		
ST/5	287/368	294/371
30/50	436/452	738/454
95/99	486/501	488/502

### Comparative Example D

2 An extrudate catalyst containing 65 wt% SSZ-32 zeolite and 35 wt%  
3 Catapal alumina binder was impregnated with 0.35 wt% Pt and crushed to 24-  
4 42 mesh (0.35-0.70 mm). After pre-sulfiding with H<sub>2</sub>S, it was used to  
5 isomerize tetracosane at 0.6 hr<sup>-1</sup> LHSV, 1000 psig (6.99 MPa), and 6.7  
6 MSCF/bbl H<sub>2</sub> (1010 std liters H<sub>2</sub>/kg oil). Results are given in Table XII,  
7 showing a 152 VI at a pour point of -9°C and a 143 VI at a pour point of -  
8 33°C.

### Example 4

Comparative Example D was repeated, except in this case, the feed was isomerized over the SSZ-32 catalyst to a pour point of +4°C, followed by solvent dewaxing to -21°C. The viscosity index (156, Table XII) was higher than in the comparative example by an estimated 8-9 numbers at the same pour point.

TABLE XII

ISOMERIZATION OF n-C<sub>24</sub>  
 AT 1000 PSIG (6.99 MPa), 0.6 hr<sup>-1</sup> LHSV,  
 AND 6.7 MSCF/BBL H<sub>2</sub> (1010 std liters h<sub>2</sub>/kg oil)  
 OVER Pt/SSZ-32 CATALYST

	Comparative Example D	Example 4
Temperature, °C	307	324
n-C <sub>24</sub> Conversion, wt%	98.9	99.8
Yields, Wt%		
C1-C2	0.3	0.3
C3-C4	4.7	5.4
C5-82 °C	7.4	8.4
82-177 °C	11.9	12.0
177-316 °C	12.2	14.8
316 °C+	63.5	59.0
316 °C+ Distillation Yield, Wt%	64.4	68.5
Solvent Dewax	No	No
Oil, Wt%		Yes
Wax, Wt%		86.1
Pour Point before SDW, °C		11.5
316 °C+ Lube Yield, Wt%	63.5	59.0
316 °C+ Lube Inspections		
Pour Point, °C	-9	-33
Cloud Point, °C	+2	-13
Viscosity, 40 °C, cSt	8.028	6.414
100 °C, cSt	2.506	2.121
VI	152	143
Avg. Branches/Molecule	1.60	
Simulated Distillation, LV%, °C		
St/5	273/333	156/240
30/50	371/383	278/373
50	387	380
70/90	390/393	383/387
95/EP	393/395	388/391

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Comparative Example E

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4 A boron-Beta zeolite was prepared according to Example 18 of US  
5 Patent No. 5,558,851. This zeolite, which had a  $\text{SiO}_2/\text{B}_2\text{O}_3$  mole ratio of  
6 about 60, was  $\text{NH}_4$ -exchanged and then impregnated with 0.5 wt% Pt. The  
7 catalyst was pelleted and crushed to 24-42 mesh (0.35-0.70 mm). After pre-  
8 sulfiding with  $\text{H}_2\text{S}$ , the catalyst was used to isomerize tetracosane at 1000  
9 psig (6.99 MPa),  $0.6 \text{ hr}^{-1}$  LHSV, and 6.7 MSCF/bbl  $\text{H}_2$  (1010 std liters  $\text{H}_2/\text{kg}$   
10 oil) to a pour point of  $+16^\circ\text{C}$ , then solvent dewaxed to a pour point of  $-18^\circ\text{C}$ .  
11 The viscosity index after solvent dewaxing was considerably lower than for  
the catalysts of this invention (Table XIII).

12

Comparative Example F

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14 0.5 wt% Pt was impregnated on an amorphous cogelled  $\text{SiO}_2$ -alumina  
15 base extrudate (31 wt%  $\text{SiO}_2$ , 69 wt%  $\text{Al}_2\text{O}_3$ ). The catalyst was crushed to  
16 24-42 mesh (0.35-0.70 mm) for testing. After pre-sulfiding with  $\text{H}_2\text{S}$ , it was  
17 used to isomerize tetracosane at 1000 psig (6.99 MPa), 0.6 LHSV, and 6.7  
18 MSCF/bbl  $\text{H}_2$  (1010 std liters  $\text{H}_2/\text{kg}$  oil) to a pour point of  $+22^\circ\text{C}$ , then solvent  
19 dewaxed to a pour point of  $-15^\circ\text{C}$ . The viscosity index after solvent dewaxing  
20 was considerably lower than for the catalysts of this invention (Table XIII and  
21 Figure 2). In addition, the isomerized and solvent dewaxed oil had a much  
higher average number of branches per molecule.

TABLE XIII  
ISOMERIZATION OF n-C<sub>24</sub>  
AT 1000 PSIG (6.99 MPa), 0.6 hr<sup>-1</sup> LHSV,  
AND 6.7 MSCF/BBL H<sub>2</sub> (1010 std liters H<sub>2</sub>/kg oil)

Catalyst	Comparative Example E Pt/B-Beta	Comparative Example F Pt/SiO <sub>2</sub> -Al <sub>2</sub> O <sub>3</sub>	Example 1 Pt/SM-3
Temperature, °C	319	329	324
n-C <sub>24</sub> Conversion, Wt%	95.2	92.4	95.1
Yields, Wt%			
C4-	2.8	0.3	0.2
C5-82 °C	5.4	1.3	0.5
82-177 °C	7.3	2.0	1.7
177-316 °C	16.6	6.7	4.3
316 °C+	67.9	89.7	93.3
316 °C+ Dist. Yield, Wt%	69.0	90.3	92.1
Solvent Dewax	Yes	Yes	Yes
Oil, wt%	86.4	86.1	65.6
Wax, wt%	13.1	11.5	32.4
Pour Point before SDW, °C	+16	+22	+20
316 °C+ Lube Yield, Wt%	58.7	77.2	61.2
316 °C+ Lube Inspections			
Pour Point, °C	-18	-15	-29
Cloud Point, °C	-13	-11	-9
Viscosity, 40 °C, cSt	8.354	8.364	8.313
100 °C, cSt	2.517	2.481	2.556
VI	136	126	148
Avg. Branches/Molecule	1.86	2.02	1.63
Simulated Dist., LV%, °C			
St/5	298/343	316/360	304/369
30/50	364/375	365/375	374/382
50	381	375	385
70/90	385/389	385/390	388/391
95/EP	390/392	391/392	392/398

## 1 WHAT IS CLAIMED IS:

- 2 1. A process for preparing an oil suitable for use as a lubricating oil base  
3 stock and having a viscosity index of greater than 140 and a target pour  
4 point of less than or equal to  $-10^{\circ}\text{C}$  comprising:
  - 5 a) contacting a waxy feed over a catalyst comprising a molecular sieve  
6 having 1-D pores with a pore diameter of between about 5.0 Å and  
7 about 7.0 Å, and at least one Group VIII metal, at a pressure of from  
8 about 15 psig (103 kPa) to about 2500 psig (13.8 MPa) to produce an  
9 isomerized oil having a pour point of at least  $6^{\circ}\text{C}$  above a target pour  
10 point; and
  - 11 b) solvent dewaxing the isomerized oil to produce a lubricating oil base  
12 stock having the target pour point and a viscosity index of greater than  
13 about 140.
- 14 2. The process according to Claim 1 for preparing a lubricating oil base  
15 stock having a target pour point of less than about  $-20^{\circ}\text{C}$ .
- 16 3. The process according to Claim 1 for preparing a lubricating oil base  
17 stock having a viscosity index of greater than 150.
- 18 4. The process according to Claim 1 wherein the waxy feed contains more  
19 than about 50% wax.
- 20 5. The process according to claim 4 wherein the waxy feed contains more  
21 than about 80% wax.
- 22 6. The process according to Claim 1 wherein the waxy feed contains more  
23 than about 70% paraffinic carbon.
- 24 7. The process according to Claim 1 wherein the waxy feed is selected from  
25 the group consisting of synthetic oils and waxes such as those by  
26 Fischer-Tropsch synthesis, high pour point polyalphaolefins, foots oils,  
27 normal alpha olefin waxes, slack waxes, deoiled waxes and  
28 microcrystalline waxes.

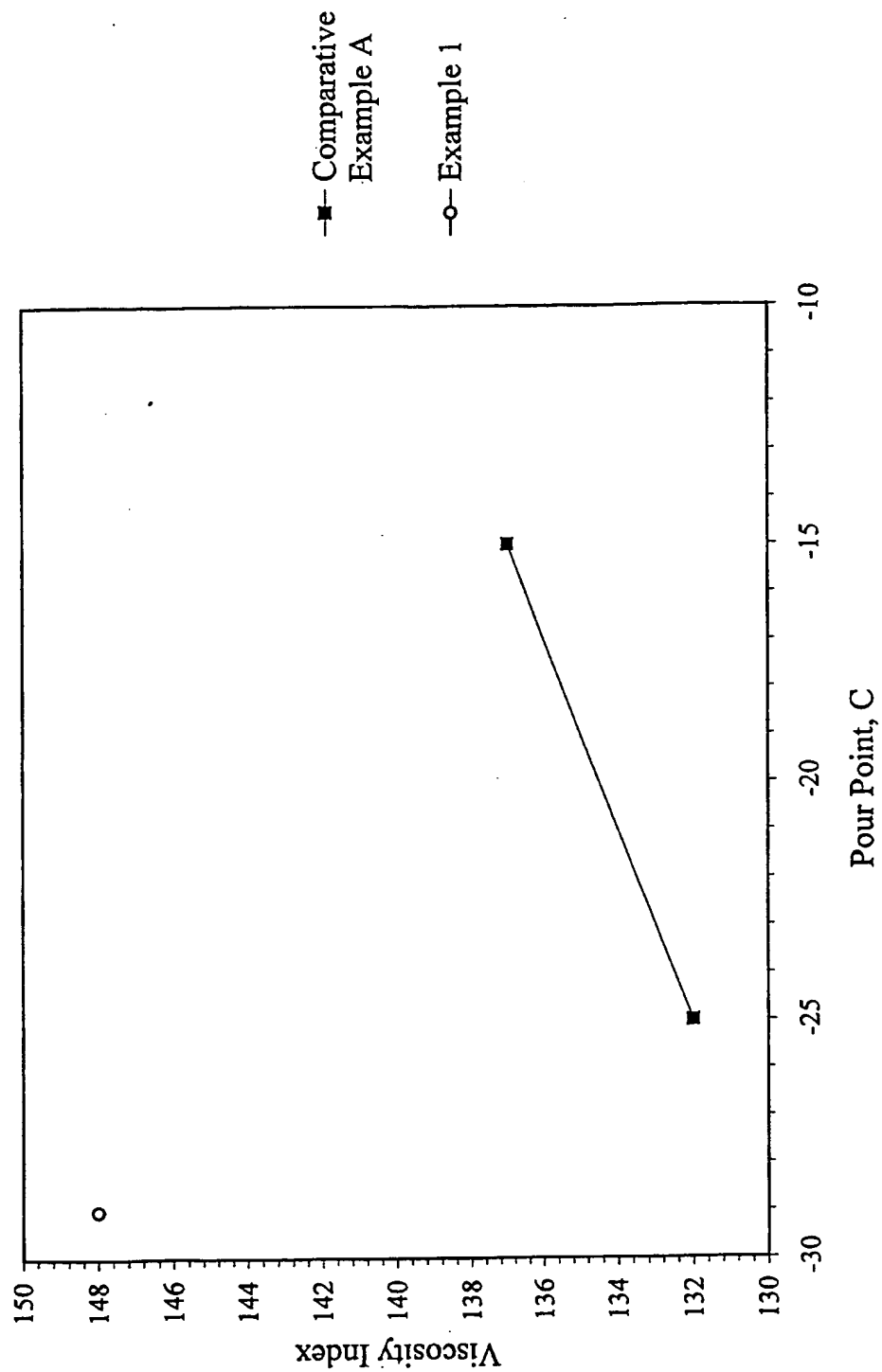
- 1    8. The process according to Claim 4 wherein the waxy feed is selected from  
2       the group consisting of synthetic oils and waxes such as those by  
3       Fischer-Tropsch synthesis, high pour point polyalphaolefins, foots oils,  
4       normal alpha olefin waxes, slack waxes, deoiled waxes and  
5       microcrystalline waxes.
- 6    9. The process according to Claim 1 wherein the isomerized oil has a pour  
7       point of greater than about 0°C.
- 8    10. The process according to Claim 1 wherein between about 60% and about  
9       99% by weight of the wax contained in the waxy feedstock is removed in  
10      step a).
- 11   11. The process according to Claim 1 wherein the medium pore molecular  
12      sieve has 1-D pores having a minor axis between about 3.9Å and about  
13      4.8Å and a major axes between about 5.4Å and about 7.0Å.
- 14   12. The process according to Claim 1 wherein the medium pore molecular  
15      sieve is selected from the group consisting of SAPO-11, SAPO-31 and  
16      SAPO-41.
- 17   13. The process according to Claim 12 wherein the medium pore molecular  
18      sieve is SM-3.
- 19   14. The process according to Claim 1 wherein the medium pore molecular  
20      sieve is selected from the group consisting of ZSM-22, ZSM-23, ZSM-35  
21      and SSZ-32.
- 22   15. The process according to Claim 14 wherein the medium pore molecular  
23      sieve is SSZ-32.
- 24   16. The process according to Claim 1 wherein the medium pore molecular  
25      sieve is ZSM-48.
- 26   17. The process according to Claim 1 wherein the hydrogenation component  
27      is a Group VIII metal selected from the group consisting of platinum,  
28      palladium or mixtures thereof.

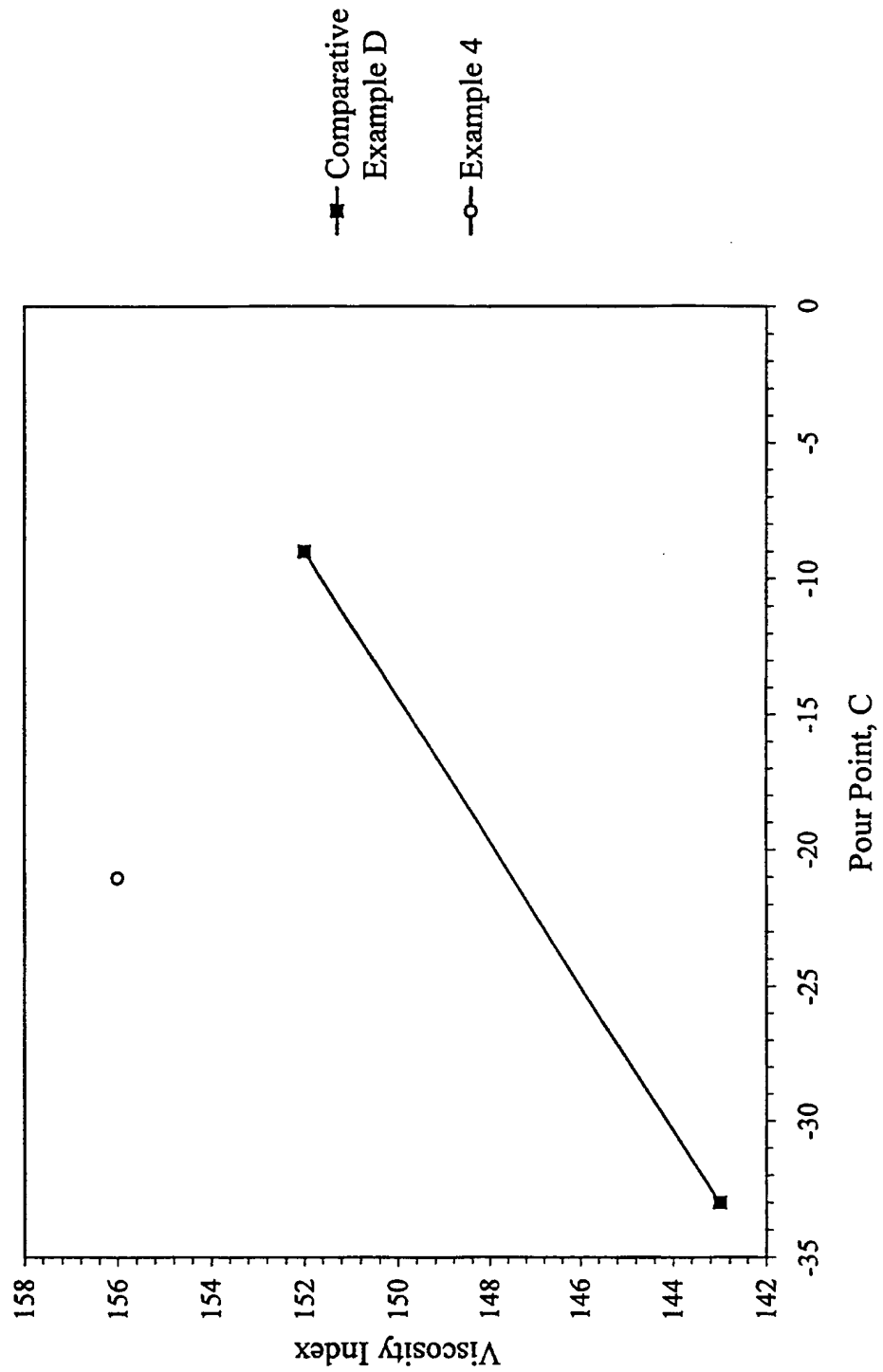


- 1 18. The process according to claim 17 wherein the catalyst contains from  
2 about 0.2% to about 1% by weight of the hydrogenation component.
- 3 19. The process of claim 1 wherein the catalyst comprising the molecular  
4 sieve has sufficient isomerization selectivity such that, when contacting a  
5 n-C<sub>24</sub> feed at a total pressure of 1000 psig (6.99 MPa), hydrogen flow  
6 equivalent to 6.7 MSCF/bbl (1010 std liters H<sub>2</sub>/kg oil), and a feed rate  
7 equivalent to 0.6 hr<sup>-1</sup> LHSV with the catalyst, to produce a 316°C+  
8 dewaxed product having a pour point of about +20°C and solvent  
9 dewaxing the dewaxed product to a pour point of -15°C or below, an  
10 isomerized product having a branching index of less than about 1.75 is  
11 formed.
- 12 20. A process for preparing an oil suitable for use as a lubricating oil base  
13 stock comprising:
- 14 a) contacting a waxy feed over a catalyst comprising a molecular sieve  
15 having 1-D pores with a pore diameter of between about 5.0 Å and  
16 about 7.0 Å, and at least one Group VIII metal, at a pressure of from  
17 about 15 psig (103 kPa) to about 2500 psig (13.8 MPa) to produce an  
18 isomerized oil having a pour point of greater than about 0°C; and
- 19 b) solvent dewaxing the isomerized oil to produce a lubricating oil base  
20 stock having a pour point of less than or equal to -10°C, a viscosity  
21 index of greater than about 140 and a viscosity, measured at 100°C, of  
22 about 3 cSt or less.
- 23 21. The process according to Claim 20 wherein the viscosity of the lubricating  
24 oil base stock, measured at 100°C, is less than about 3 cSt and the pour  
25 point is less than or equal to -20°C.
- 26 22. The process according to Claim 20 wherein the viscosity index of the  
27 lubricating oil base stock is greater than 150 and the pour point is less  
28 than -20°C.
- 29 23. The process according to Claim 20 wherein the molecular sieve is  
30 SSZ-32.

- 1 24. The process according to Claim 20 wherein the molecular sieve is SM-3.
- 2 25. A lubricating oil base stock having a viscosity index of at least about 140,
- 3 a pour point of less than or equal to  $-10^{\circ}\text{C}$ , and a viscosity, measured at
- 4  $100^{\circ}\text{C}$ , of about 3 cSt or less.
- 5 26. The lubricating oil base stock of Claim 25 having a viscosity index of at
- 6 least about 150 and a pour point of less than or equal to  $-20^{\circ}\text{C}$ .
- 7

Figure 1



**Figure 2**

# INTERNATIONAL SEARCH REPORT

International Application No

PCT/US 99/02121

**A. CLASSIFICATION OF SUBJECT MATTER**  
IPC 6 C10G67/04 C10G45/64

According to International Patent Classification (IPC) or to both national classification and IPC

**B. FIELDS SEARCHED**

Minimum documentation searched (classification system followed by classification symbols)  
IPC 6 C10G

Documentation searched other than minimum documentation to the extent that such documents are included in the fields searched

Electronic data base consulted during the international search (name of data base and, where practical, search terms used)

**C. DOCUMENTS CONSIDERED TO BE RELEVANT**

Category *	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
X	US 4 919 788 A (CHEN NAI Y ET AL) 24 April 1990  see claims 1-9	1-10, 17-22, 25, 26
Y	---	11-16, 23, 24
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☒ Further documents are listed in the continuation of box C.

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Date of the actual completion of the international search

26 April 1999

Date of mailing of the international search report

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# INTERNATIONAL SEARCH REPORT

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## C.(Continuation) DOCUMENTS CONSIDERED TO BE RELEVANT

Category *	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
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# INTERNATIONAL SEARCH REPORT

Information on patent family members

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